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Reaction rates for collisional de-excitation of
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[_u] state of N [⁺]
[₂] and the C [³(pi)
[_u] state of N [₂]

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OF THE $B^2 \Sigma_u^+$ STATE OF N_2^+ AND THE $C^3 \pi_u$
STATE OF N_2

by

Allan Ray Smelley

United States Naval Postgraduate School



THESIS

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Reaction Rates for Collisional De-excitation

the $B^2\Sigma_u^+$ State of N_2^+ of and the $C^3\Pi_u$ State of N_2

by

Allan Ray Smelley

Lieutenant, United States Navy

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Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

from the

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June 1969

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SMELLEY, A.

ABSTRACT

Pure nitrogen and nitrogen-oxygen gas mixtures at pressures from 1 to 800 torr and 300° K were excited by 1.5 MeV protons. Intensity versus pressure data were recorded and plotted for the first negative ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) transition ($\lambda = 3914.4 \text{ \AA}$), and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) transition ($\lambda = 3371.3 \text{ \AA}$) in nitrogen. Theoretical equations were derived for the intensity as a function of pressure, which were shown to agree quite well with the experimental data. The following reaction rates, k , and de-excitation cross sections, σ , were obtained from the derived theoretical equations and the experimental data: $k = (2.19 \pm 0.29) \times 10^{-10} \text{ cm}^3/\text{sec}$ and $\sigma = (3.25 \pm 0.45) \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $B^2\Sigma_u^+$ state of N_2^+ by N_2 ; $k = (5.70 \pm 0.80) \times 10^{-10} \text{ cm}^3/\text{sec}$ and $\sigma = (8.47 \pm 1.26) \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $B^2\Sigma_u^+$ state of N_2^+ by O_2 ; $k = (7.11 \pm 1.64) \times 10^{-12} \text{ cm}^3/\text{sec}$ and $\sigma = (1.06 \pm 0.25) \times 10^{-16} \text{ cm}^2$ for the de-excitation of the $C^3\Pi_u$ state of N_2 by N_2 ; and $k = (4.62 \pm 0.67) \times 10^{-10} \text{ cm}^3/\text{sec}$ and $\sigma = (6.85 \pm 1.10) \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $C^3\Pi_u$ state of N_2 by O_2 .

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I. INTRODUCTION

Studies on the excitation of nitrogen (N_2) by proton impact is of astrophysical interest. In this study the formation of N_2^* and $(N_2^+)^*$ under proton impact on research grade nitrogen were investigated. Proton impact on nitrogen with oxygen (O_2) present was also investigated. In particular, the first negative transition ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) wave length ($\lambda = 3914.4 \text{ \AA}$) and the second positive transition ($C^3\Pi_u \rightarrow B^3\Pi_g$) ($\lambda = 3371.3 \text{ \AA}$) were used to study and measure reaction rate coefficients and de-excitation cross sections for the reactions $(N_2^+)^* + N_2 \rightarrow N_2^+ + N_2 + \text{energy}$ and $(N_2)^* + N_2 \rightarrow 2N_2 + \text{energy}$. The impact energy range was from 1.0 to 2.0 MeV. A lower energy range up to about 1.5 MeV has been measured by Reeves, Nicholls, and Bromley [Ref. 1]; Sherridan and Clark [Ref. 2]; Roesler, Fan, and Chamberlain [Ref. 3]; and Robinson and Gibbody [Ref. 4], but these papers only considered the situation where the pressure was low enough such that the single hit condition [Ref. 5] applied, and these authors measured the excitation cross sections, or the rotational band temperatures. In this study the pressure was varied from 1 to 800 torr in all cases. The single hit condition does not apply at such high pressures.

The experiment was carried out to find the relationship between pressure and intensity as the pressure was varied from 1 to 800 torr. From the experimental data, collisional de-excitation cross sections and reaction rate coefficients were calculated which agree with values found in the DASA Reaction Rate Handbook [Ref. 6] (Ch. 15, 19).

II. EXPERIMENTAL PROCEDURE

A 2.5 MeV Van De Graaff was used to accelerate protons into a target chamber where the gas pressure could be varied from a minimum value of about 2×10^{-6} torr to 800 torr. Figure 1 is a schematic diagram of the experimental apparatus. In order to keep the Van De Graaff and its associated drift tube under the 10^{-6} torr vacuum necessary for efficient operation a thin aluminum window approximately 5.0×10^{-4} inches thick was placed between the target chamber and the drift tube. The energy loss by the proton beam in passing through this window was 0.25 ± 0.05 MeV. This energy loss was measured by using a lithium fluoride target and a neutron counter. The presence of the aluminum foil window allowed the target gas pressure to be varied independently of the vacuum in the Van De Graaff. The target gas was fed into the target chamber via a high pressure regulator, needle valve, and manifold system. The actual pressure was measured by two Wallace and Tiernan pressure gauges, one with a scale reading from 0-50 torr, and one from 0-800 torr.

The target chamber's vacuum system consisted of an oil diffusion pump, as well as an independent fore pump. The vacuum was measured by thermo couples and ion gauges.

The target gas was excited and ionized by a proton beam of about 2.0 microamps and energy from 1.0 to 2.0 MeV. The beam current was collected by a faraday cup and the total beam charge was measured by an Eldorado Electronics, model CI-110 current intergrator.

The intensity of the excited target gas was measured at 90° from the proton beam. The light was focused by a 15 cm focal length quartz lens through a mechanical chopper into the slits of a Jerral Ash monochrometer.

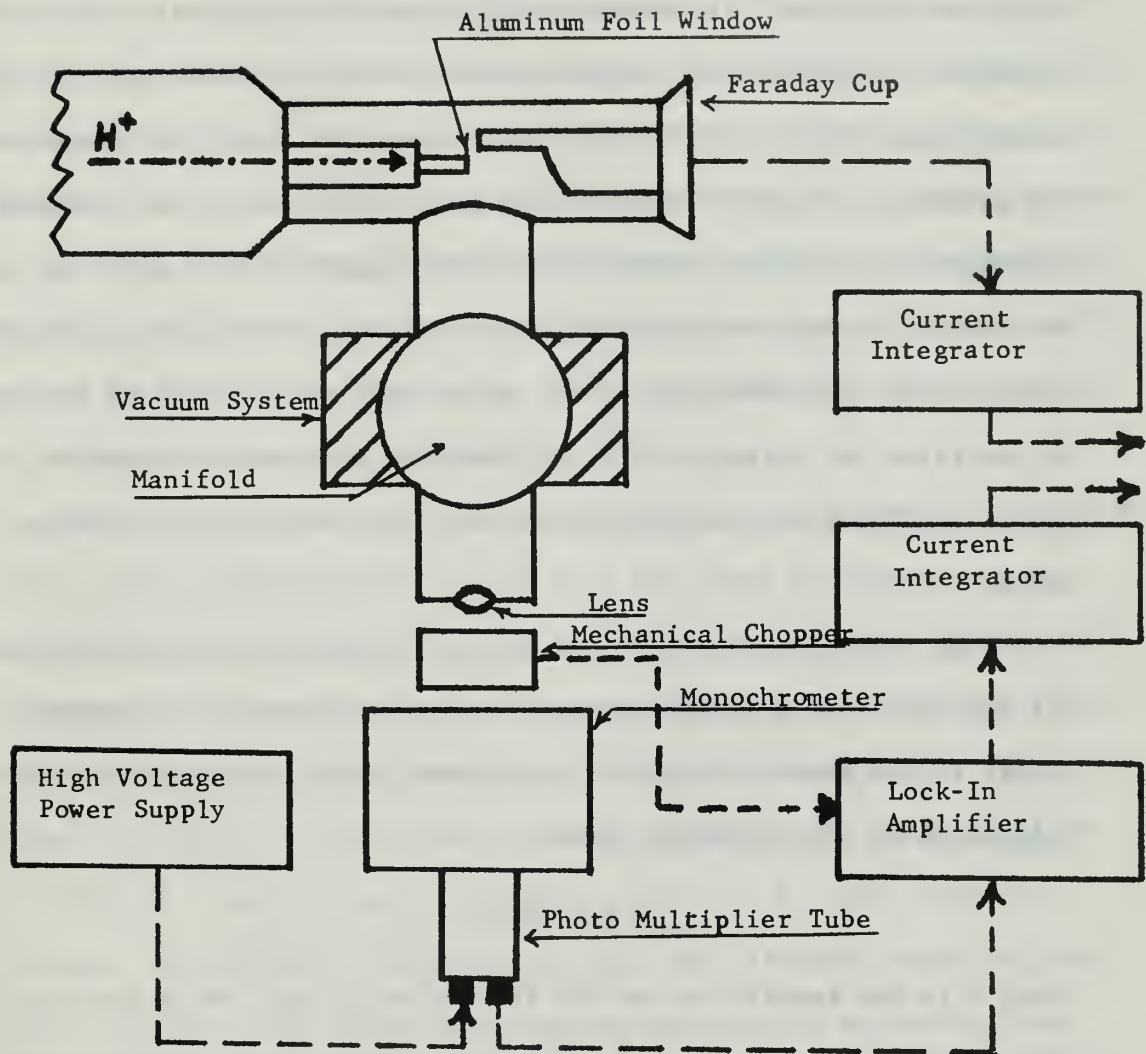


FIGURE 1. Collision Chamber, Optical Apparatus, and Electronics Schematic.

The light passed from the monochrometer into an Electro Optics Associates, type PM-101 photo multiplier tube assembly with 7102 PM tube where the light was converted into an electrical signal proportional to the light's intensity. The electrical signal was fed into a Princeton Applied Research, model HR-8, lock-in amplifier, where the signal was compared to the mechanical chopper's reference signal. The chopper was operated at a frequency of 78 hertz. The mechanical chopper/lock-in amplifier system was used to convert the light intensity into an AC current, eliminating dark current considerations of the photo tube. The output of the lock-in amplifier was integrated by an identical Eldorado Electronics, model CI-110 current integrator that was used to measure total beam charge.

Using the apparatus described above, intensity (I) versus pressure (P) data were recorded and plotted. Since the intensity is proportional to the photo multiplier tube current (PH), the intensity was calculated in the following manner.

$$\underline{I} = S \times PH/B$$

where S is the sensitivity of the lock-in amplifier, PH is the total photo charge collected, and B is the total proton beam charge collected. The value of B was chosen to be always 50 microcoulombs of charge, and PH also in microcoulombs, was measured over the same time interval for each value of pressure. Hence, I is a relative intensity in arbitrary units. The pressure of the target gas was varied from 1 to 800 torr and I was measured for each pressure considered. The target gases were nitrogen and nitrogen-oxygen mixtures. With the aid of an IBM 360 computer, intensity versus pressure curves were plotted for the various experimental data, Figs. 2, 3, 4, and 5. Both the molecular nitrogen

second positive and first negative band systems were used. The light emitted by the excited target gases was focused by a 15 cm focal length quartz lens on the slits of the monochromator. These slits, which are 2 cm's long and 0.8 mm wide, were perpendicular to the proton beam path, and were positioned such that only the light coming 1 to 2 mm from the aluminum foil window was passed into the monochromator. The energy loss in the beam was very small over this distance, especially when compared to the energy loss in the beam that would be measured if the slits were placed parallel to the beam path. Thus the energy loss in the beam and secondary processes were minimized.

The resolving power of the monochromator was $\pm 15\text{\AA}$ about the central wave length being measured. Great care was taken to ensure that no other molecular or atomic line was within 15\AA of the lines considered. Photographs of the molecular nitrogen spectrum, using a Gaertner L 254 quartz spectrometer and 70 mm Kodak 2485 high speed film were taken from 2000-8000 \AA . On the plates of pure nitrogen, the first negative $\lambda = 3914.4\text{\AA}$, and the second positive, $\lambda = 3371.3\text{\AA}$, were the most intense. Photographs of nitrogen-helium, and nitrogen-oxygen mixtures were also made. The presence of helium enhanced all molecular band structure of nitrogen, especially the first negative system; conversely the presence of oxygen caused a marked decrease in the intensities of the N_2 spectrum. The helium spectrum was easily photographed, but all attempts to photograph the pure molecular oxygen spectrum were completely unsuccessful even with exposure times up to 3 hours. The exposure time for 100% N_2 or N_2/He mixtures were as short as $\frac{1}{2}$ hour with excellent results. Another interesting result was that none of the first positive molecular nitrogen band system ($\text{B}^3\Pi_g \rightarrow \text{A}^3\Sigma_u^+$) transitions nor any atomic hydrogen lines were detected.

A study of the data presented in Fig. 2, 3, and 5 verifies completely what was displayed on the photographs of the N_2 , N_2/O_2 mixture spectrum. It is easily seen from Figs. 2, 3, and 5 that as the amount of O_2 is increased in the target chamber, the relative intensity decreases in a corresponding manner. The basic shape of the pressure versus intensity curves remains the same; that is, the intensity rose sharply over the first few torr of pressure and then leveled off to a nearly constant value after about 75 torr of pressure.

III. THEORY

A. BACKGROUND

In view of the experimental results that were obtained, an attempt was made to develop a set of theoretical equations that would give results in good agreement with the experimental data. The following general rate equation [Ref. 7] was the foundation from which the theoretical equations were developed.

$$\frac{dN_k^*}{dt} = 0 = R_k + \sum_{l>k} \lambda_{lk} N_l^* - \sum_{k>i} \lambda_{ki} N_k^* - \sum_j N_k^* K_{kj} n_j + \sum_m n_m^* K_{mk} n_k \quad (1)$$

Where 1: R_k direct excitation to state k by protons (H^+).

2: $\sum_{l>k} \lambda_{lk} N_l^*$ transitions from higher state l into state k .

3: $\sum_{k>i} \lambda_{ki} N_k^*$ loss by transitions from state k to state i .

4: $\sum_j N_k^* K_{kj} n_j$ collisional de-excitation of state k with particles n_j .

5: $\sum_m n_m^* K_{mk} n_k$ excitation to state k by collisions with atoms in excited state n_m .

and, N^* - density of excited particles per volume in state k.

λ_{ki} - decay probability from state k to state i (sec^{-1}).

K_j - reaction rate (cm^3/sec).

In order to get equation (1) into a usable form, the following assumptions were made:

- 1: N^* proportional to Intensity (I).
- 2: R_k proportional to Pressure (P) in the target chamber.
- 3: n_j proportional to Partial pressure (P_j).
- 4: $\sum_k \lambda_{ki} = \lambda$ constant for the line in question.
- 5: $\sum_j K_j = K$ constant for the line in question.
- 6: The ideal gas law $PV = NRT$ was the equation of state for the gases in the target chamber.

At this point a discussion of the reactions involved within the target chamber and a discussion of the assumptions made are in order. Since nitrogen gas or nitrogen-oxygen gas mixtures were the target gases, the following primary reactions could occur in the target chamber:



The de-excitation of the excited states of N_2^+ and N_2 and the role O_2 plays will be discussed in more detail in later sections. In the DASA Reaction Rate Handbook [6] (Ch. 4-15), almost all of these possible de-excitation mechanisms are discussed in detail and this handbook was invaluable for the theoretical development of this paper.

The protons (H^+) excited the target gases directly to an arbitrary energy state k as well as many other states above and below state k . The assumption that R_k is directly proportional to target gas pressure, vital to this development, is valid if no population of energy state k occurs for higher states due to x-ray cascade.

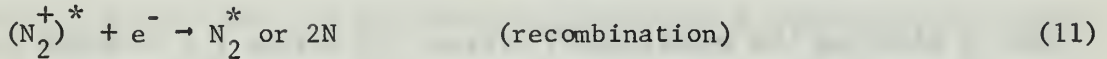
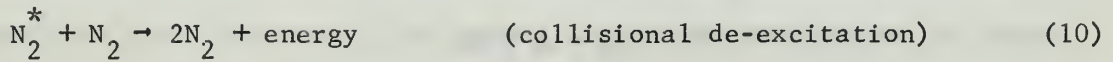
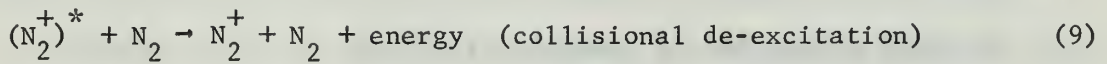
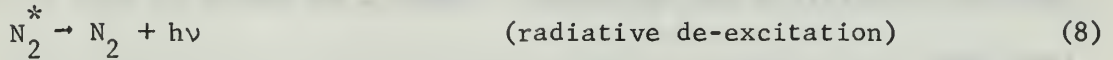
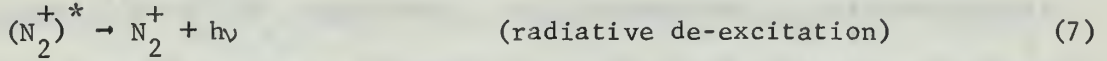


That is, the projectile protons can easily knock out K, L, or M shell electrons from a gas molecule, and x-rays are a possible result. Thus the assumption that R_k is directly proportional to target pressure depends on the radiative lifetime of the x-rays being much much shorter than the time between collisions ($\tau_{\text{coll.}}$) of the molecules in the target gas. The time between collisions in a gas has been calculated for N_2 gas at 1 atm. by Reif [Ref. 8] and $\tau_{\text{coll.}} \cong 6 \times 10^{-10}$ secs. The mean radiative lifetime of an x-ray is known to be on the order of 10^{-12} to 10^{-15} secs. For N_2 gas $\tau_{\text{x-ray}} \cong 10^{-13}$ secs. [Ref. 9]. Thus, $\tau_{\text{x-ray}} \ll \tau_{\text{coll.}}$ and R_k is proportional to pressure.

Many thermodynamics text books [Ref. 10] have shown that the ideal gas law holds out to several atmospheres of pressure for most atmospheric gases; hence, the assumption that the ideal gas law is the correct equation of state is certainly valid to a high degree. From the ideal gas law $P_j = n_j k T$, the partial pressure of gas j is directly proportional to n , the number of molecules of type j per cm^3 in the target gases.

B. NITROGEN AS THE TARGET GAS

One hundred percent research grade nitrogen was used as the target gas, and the resulting bombardment by protons created excited states in N_2 gas, equations (2) and (3). The primary mechanisms for de-excitation of these excited states are as follows:



From the general equation (1) a specific equation that attempts to explain the behavior of the de-excitation of $(N_2)^*$ and $(N_2^+)^*$ in view of equations (7), (8), (9), and (10) is deduced, if one applies the assumptions that R_k is proportional to target gas pressure and N^* is proportional to intensity, then $dN_k^*/dt = 0 = C'P - A'I - B'PI$, or,

$$P = \frac{A'I}{C' - B'I} \quad (12)$$

where it is assumed that all summations have been performed and A and B are constants to be determined.

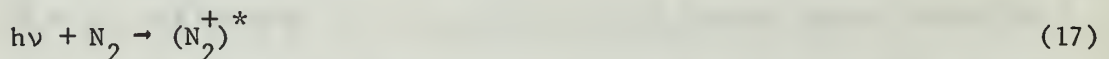
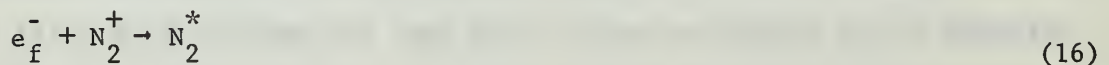
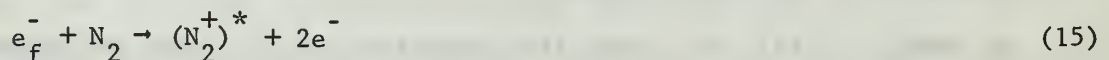
In equation (12), two terms from equation (1) have been neglected by assuming that a transition exist, such that the population of state k from higher energy states $k + 1$, $k + 2$,, is negligible (term #2) and that excitation by collisions with excited molecules due to pressure is also negligible (term #5). These assumptions are shown to be reasonable by noting that the temperature of the target gases is very close to room temperature [1,3,4]. The r.m.s. velocity (V_{rms}) of the target gases

have a Boltzman distribution $\rightarrow V_{\text{rms}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$, with $E = \frac{1}{2} mv^2$, so that $E = 3/2 kT$. The maximum possible energy transfer between two molecules could never be more than $2E$ or $E_{\text{max}} \cong 3 kT$. Since kT at room temperature is on the order of $1/40$ of an eV, the energy available is much smaller than the energy required to remove an optical electron from a nitrogen molecule. For example, for a wavelength of 3914.4\AA (first negative transistion for molecular nitrogen), an energy of over 3 eV is required.

Dividing both sides of equation (12) by \underline{I}

$$P/\underline{I} = A + BP \quad (13)$$

Thus by plotting the experimental data as P/\underline{I} versus P a straight line of slope B and intercept A should result. This was indeed the case as shown in Fig. 4, at pressures below 100 torr. At higher pressures the P/\underline{I} vs P plot varies slowly from linearity. To better explain the data, a corrective term to equation (12) must be applied. The linearity of the data to about 100 torr would suggest that above this pressure secondary processes are taking place in the target chamber that are not negligible. The following mechanisms of N_2 excitation could also occur:



Where e_f^- is a fast electron from delta rays produced by the primary particle.

To show that the electrons (e_f^-) in equations (14), (15), and (16) have enough energy to cause secondary excitation of N_2 , one must calculate the maximum energy that a proton of energy E_p can transfer to a

bound electron of a nitrogen molecule. The maximum binding energy of a K shell electron in N_2 was found to be on the order of 400 eV [9]. Thus the proton must transfer this much energy plus at least enough kinetic energy (E_e) to the electron to cause secondary excitation of N_2 . The maximum energy transferred from the proton to a free electron can be found, $E_e \cong \frac{4m_e m_p}{(m_e + m_p)^2} E_p$. Thus for a 1.5 MeV proton, $E_e \cong 4(m_e/m_p) E_p = 4E_p/1837 \cong 3300$ eV. Hence, it is easily seen that secondary ionization and excitation can take place due to secondary electrons.

Equation (17) also must be considered, as the photons ($h\nu$) can have energies up to the soft x-ray range, as already calculated, to about 400 eV; hence, possibly secondary excitation of N_2 molecules by x-rays.

Since the production of electrons as well as photons (x-rays) in equations (2), (3), (5), and (6) are proportional to pressure, the mechanisms for production of $(N_2^+)^*$ and (N_2^*) as suggested by equations (14) through (17) will be proportional to P^2 . To allow for the above mechanisms in equation (1), the parameter R_k must have a term proportional to pressure squared; thus, equation (12) becomes with $R_k \rightarrow C'P + C''P^2$,

$$P = A\underline{I} + B\underline{P\underline{I}} - CP^2 \quad (18)$$

where C is a small constant to be determined, and CP^2 is a small correction.

Equation (18) was used as the basis for least squares curve fitting to the data previously obtained for 100% pure nitrogen gas. The actual computations and graphs were done by an IBM 360 digital computer. All three constants A , B , and C were calculated, and a smooth curve was superimposed upon the actual data points. Figs. 6 and 7 are typical results for the first negative ($\lambda = 3914.4\text{\AA}$), and second positive ($\lambda = 3371.3\text{\AA}$) lines of molecular nitrogen. There is excellent agreement of the data and the theoretical equation (18).

Since the theory developed appeared to be reliable, and more than adequately described the actual de-excitation of $(N_2^+)^*$ and $(N_2)^*$, the product of the reaction rate and the radiative lifetime (τ) of the line in question could be determined. This was done as follows; since equations (7), (8), (9), and (10) are the assumed mechanisms for de-excitation of $(N_2^+)^*$ or $(N_2)^*$, then equation (12) is the correct equation from which to determine the product $(\tau) \times (K)$. This is more easily understood by noting that the CP^2 term in equation (18) is a measure only of the secondary excitations of $(N_2^+)^*$ and $(N_2)^*$. Consequently, if there were no secondary excitation of (N_2) or (N_2^+) then equation (12) would hold over the entire target gas pressure ranges. Equation (12) $P = A\underline{I} + B\underline{P}\underline{I}$, or equation (12a) $R_k = \lambda_{ki} N_k^* + K_j n_j$ (dropping summation signs). With the use of the ideal gas law $P_j = n_j kT$, $R = aP$, $(N_k^*) = b\underline{I}$; substituting into (12a) $P = \frac{b}{a} \underline{I} + \frac{b}{a} \underline{I} K \frac{P}{kT}$; comparing equations (12) and (12a) and equating constants, one sees that $A = \frac{b}{a}$ and $B = \frac{bK}{akT}$. By taking the ratio of $\frac{B}{A}$ the value of K (the reaction rate) or (the mean radiative lifetime) τ can be determined.

$$K = \frac{B}{A} \frac{kT}{\tau} \quad (19)$$

A dimensional analysis of equation (12) yields the units of A to be ($\text{sec} - \text{cm}^{-3}$) and B to be ($\text{sec} - \text{erg}^{-1}$) which agrees with equation (19). Since there is one equation with two unknowns, K and τ , it was decided to calculate the reaction rate from equation (19); hence, the value of τ had to be found from the literature pertinent to the subject. Bennett and Dalby [Ref. 11] experimentally found the values of τ for the first negative (3914.4\AA) and second positive (3371.3\AA) systems. These values can be compared to values tabulated by Nicholls [Ref. 12] which were theoretically derived. Table I contains the comparisons.

Reference	λ (Å)	$\tau \times 10^{-8}$ sec's
11	3914.4	6.58
12	3914.4	8.06
11	3371.3	4.45
12	3371.3	9.00

TABLE I. Radiative Lifetimes

The experimentally obtained values of Bennett and Dalby were the ones used to calculate K as it was felt that they were more accurate. Hence, the uncertainty in K is certainly not any better than the uncertainty in τ .

The collisional de-excitation cross section (σ_d) can be calculated from $N^* K_j n_j = N^* \sigma_d \varphi_j$ where φ_j equals the flux of particles of type j and σ_d is the probability that a de-excitation collision will occur. But $\varphi_j = \bar{V}_r n_j$ where \bar{V}_r is the mean relative velocity (5) between molecules. Thus $N^* K_j n_j = N^* \sigma_d \bar{V}_r n_j$, or

$$\sigma_d = K_j / \bar{V}_r \quad (20)$$

where \bar{V}_r is

$$\bar{V}_r = \left[\frac{8kT}{\pi} \frac{(m_1 + m_2)}{m_1 m_2} \right]^{\frac{1}{2}} \quad (21)$$

for a mixture of two gases in thermal equilibrium. For 100% nitrogen gas

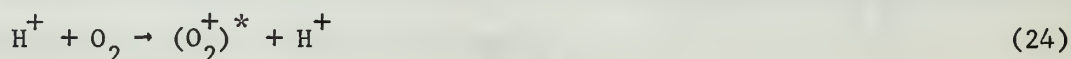
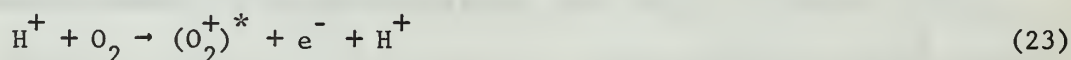
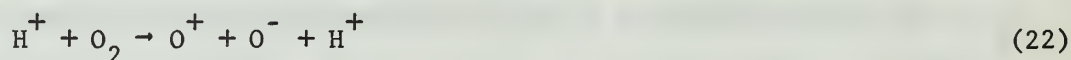
$$\bar{V}_r = \left(\frac{16kT}{\pi m} \right)^{\frac{1}{2}} \quad (21a)$$

Using equations (18), (19), and (20) the reaction rates (K_j) (21a) and collisional de-excitation cross sections (σ_d) were calculated for N_2 gas. The results are tabulated in Table II. The ratio of B/A must be constant to within experimental error for each set of experimental data.

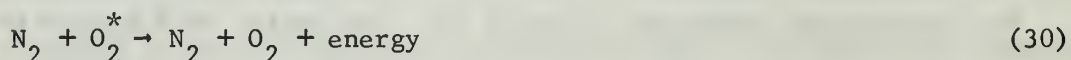
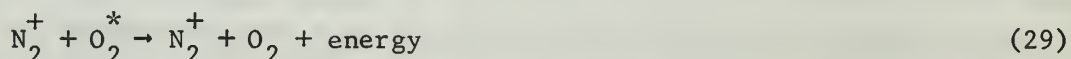
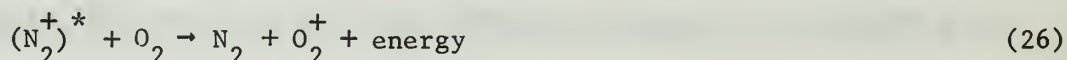
The values of the constants A and B did vary somewhat between different experimental runs due to slight variations in the experimental apparatus, but their ratio's did remain invariant to within experimental error over six experimental runs.

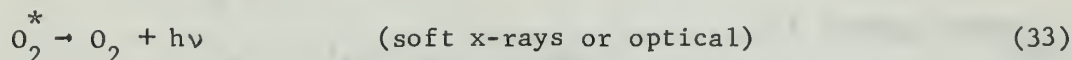
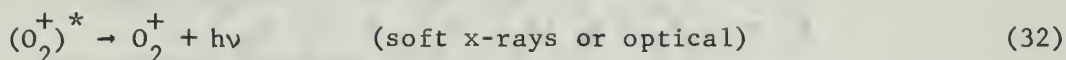
C. NITROGEN WITH OXYGEN PRESENT

The results obtained with the experimental set-up and the agreement between theory and the experimental data using 100% nitrogen as the target gas were excellent. Nitrogen at a constant partial pressure (P_{N_2}), with oxygen then added to increase the total pressure (P) in the target chamber up to 800 torr, was investigated. Equations (2), (3), and (4) are the primary means of direct excitation to state k, due to proton bombardment. Other possible direct excitations due to proton bombardment are:

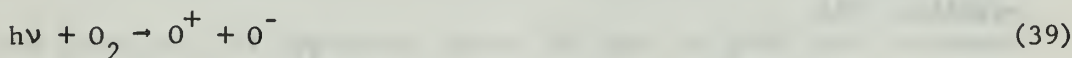


The de-excitation of excited state k, occurs, equation (7), (8), (9), and (10) as well as by:





Secondary processes that cause excitation take place by equations (5), or (6) plus,



The experimental data Fig. 5 indicated that there is a rather large mechanism for de-excitation of excited states of nitrogen when oxygen is present. The excited states of oxygen certainly must exist, but all attempts made to photograph the molecular oxygen spectrum were unsuccessful. Thus, the conclusion was made that the excited states of oxygen are negligible compared to those in nitrogen. From the inability to detect the O_2 spectrum and inspection of the experimental data Figs. 3 and 5 it was postulated that the presence of oxygen in the target chamber quenches the $(N_2^+)^*$ and $(N_2^+)^*$ states by a much larger collisional de-excitation rate K , than the collision de-excitation rate when only nitrogen is in the target chamber. The results displayed in table 15-6 in the DASA Reaction rate Handbook (July 1967) [6] indicate this is true for the $(N_2^+)^*$ de-excitation.

Using equation (1) in the same manner as before, with

$$R_k = \lambda_{ki} N_k^* + N_k^* (K_j^{N_2} n_j^{N_2} + K_j^{O_2} n_j^{O_2}) \quad (41)$$

which reduces to,

$$P = A\underline{I} + (BP_{N_2} + EP_{O_2})\underline{I} \quad (42)$$

Equation (42) suggest a simple way to determine the undetermined constant E. First collect experimental data using 100% N_2 as the target gas up to 100 torr pressure (P_{N_2}). Since secondary processes are negligible at pressure lower than 100 torr, equation (12) can be used to calculate the constants A and B in the manner previously discussed. At this point in the experiment 100% pure oxygen was added, P_{N_2} was kept constant, and pressure versus intensity data was recorded. Using equation (42),

$$E = \left[P_{N_2} - (A + BP_{N_2})\underline{I} / P_{O_2} \underline{I} \right] \quad (43)$$

where P_{N_2} , A, and B are known constants and $P_{O_2} = P - P_{N_2}$ which is the partial pressure of oxygen in the target chamber.

The collisional de-excitation reaction rates (K_{N_2}) and (K_{O_2}) can be determined by comparing equations (44) and (42) in the same manner as was the case for determining K for the 100% N_2 case; or,

$$K_{O_2} = E/A \frac{kT}{\tau} \quad (44)$$

It also follows that the collisional de-excitation cross section for equations (25), (26), (27), and (28) are equal to $\sigma_d = K_{O_2} / \bar{v}_r$ where \bar{v}_r is given by equation (21). A comparison of the two reaction rates and equation (42) shows that for any given experimental run,

$$K_{O_2} / K_{N_2} = E/B \quad (45)$$

K_{O_2} was found to be approximately 2.6 times as large as K_{N_2} for first negative transitions.

By rearranging equation (42),

$$\underline{I} = P_{N_2} / \left[(A + BP_{N_2}) + EP_{O_2} \right] \quad (46)$$

Since the only variables are \underline{I} and P_{O_2} , as P_{O_2} increases \underline{I} must decrease. This agrees with Fig. 5. Fitting the experimental data to equation (42) was carried out with the aid of an IBM 360 digital computer with the result shown in Fig. 8. The remarkably good fit of equation (46) to the experimental data would seem to vindicate the earlier postulates; that the presence of O_2 quenches N_2 excited states, and that no secondary effects are taken into effect by equation (42). This is not unreasonable since, as was shown earlier, secondary excitation effects only became barely noticeable at pressures above 100 torr in 100% pure nitrogen. Since, (a) the nitrogen pressure (P_{N_2}) was constant at 100 torr; (b) excited states of oxygen were not even detected by the spectrometer (as discussed earlier); and (c) the reaction rate for O_2 de-excitation is at least a factor of 2 larger than the reaction rate of N_2 ; it is seen that secondary effects are negligibly small.

D. NITROGEN-OXYGEN MIXTURES

Another method of observing the effects that O_2 has on N_2 in the target chamber was observed by bombarding N_2/O_2 mixtures by protons. Fig. 3 graphically displays experimental data for the second positive nitrogen band system ($\lambda = 3371\text{\AA}$). The mixtures were kept at a constant percentage such that $P = P_{N_2} + P_{O_2}$ and $P_{N_2} = nP$; $P_{O_2} = oP$ where $n + o = 1$. Only slight modifications to equation (18) are required to develop an applicable theoretical equation.

$$nP = A\underline{I} + Bn\underline{PI} + E_O\underline{PI} - n^2 CP^2, \quad (47)$$

or

$$P = \frac{A}{n} \underline{I} + B\underline{PI} + \frac{E_O}{n}\underline{PI} - nCP^2 \quad (47a)$$

The data and theory were compared in the usual manner. Typical results as displayed by Fig. 9 indicate again the theoretical equations developed for the nitrogen/nitrogen-oxygen mixtures are valid to a high degree of accuracy. The same argument applies as before for not including a term in equation (47) due to direct excitation of O_2 molecules due to bombardment by protons (R_k). It is admitted that the addition of these terms should yield a finite correction to equation (47). The correction between equations (12) and (18) due to secondary processes (the CP^2 term) is less than 10%. And since experimental results using photographic techniques, as well as the earlier discussed results concerning direct and secondary excitation of oxygen molecules; all indicated that excited states of oxygen (O_2)^{*} are several orders of magnitude smaller in intensity than excited states of (N_2^+)^{*} or (N_2)^{*}. Consequently, the neglect of the extremely small contributions in the R_k term due to the partial pressure of oxygen in equation (1) is justified to a high degree, especially since only molecular nitrogen lines are being observed.

Table II is a summary of the ratio's (B/A) and (E/A), reaction rates (K_{N_2}) and (K_{O_2}), collisional de-excitation cross sections (σ_{N_2}) and (σ_{O_2}), and a comparison with reaction rates located in DASA Reaction Rate Handbook [6] (Ch. 15).

De-excitation Reaction	Ratio $\text{cm}^3 \text{ erg}^{-1}$	K $\text{cm}^3 \text{ sec}^{-1}$	σ_d cm^2	K[Ref 6] $\text{cm}^3 \text{ sec}^{-1}$
$\text{N}_2^{+*}(\text{B})$ by N_2	$^{+}(4.63 \pm 0.26) [-1]$	$(2.19 \pm 0.29) [-10]$	$(3.25 \pm 0.45) [-15]$	$(6.0) [-10 \pm 1]$
$\text{N}_2^{*}(\text{C})$ by N_2	$(1.02 \pm 0.11) [-2]$	$(7.11 \pm 1.64) [-12]$	$(1.06 \pm 0.25) [-16]$	
$\text{N}_2^{+*}(\text{B})$ by O_2	$(1.21 \pm 0.10) [0]$	$(5.70 \pm .80) [-10]$	$(8.47 \pm 1.26) [-15]$	$(2.0) [-9 \pm 1]$
$\text{N}_2^{*}(\text{C})$ by O_2	$(.661) [0]$	$(4.62 \pm .67) [-10]$	$(6.85 \pm 1.10) [-15]$	
$^{+}(4.63 \pm 0.26) [-1] = (4.63 \pm 0.26) \times 10^{-1}$				

TABLE II. Reaction Rate's (K) and De-excitation Cross Sections (σ_d)

IV. RESULTS

A. TEMPERATURE DEPENDENCE

Temperature measurements were not made for this experiment. The rotational band temperatures have been measured and the results reported in other papers. Reeves, Nicholls, and Bromley [1] measured the N_2 first negative system (3914\AA) rotational temperature under impact of 1.0 MeV protons and obtained a value of $T = 276^{\circ} \pm 10^{\circ}\text{K}$. This value agreed with their laboratory temperature to within 5°K . Similar agreement was obtained between laboratory temperatures and rotational temperatures of the N_2 bands excited by 10 and 30 keV protons, Roesler, et.al., 1958 [3] and 10 to 65 keV ions, Sheridan and Clark [2]. The measurements taken by Reeves, Nicholls, and Bromley showed agreement between gas kinetic and rotational temperatures at particles energies above 500 keV and showed there was no appreciable interaction between the bombarding particle (H^+) and the internal motion of the target molecule. The good agreement of all the above experimental evidence justified the use of room temperature as the most correct value for temperature in equations (19) and (21).

B. PRESSURE DEPENDENCE

Reeves, Nicholls, and Bromley indicated a sharp rise in intensity with pressure, at pressures above 0.6 torr. From 0 to 0.6 torr they reported a linear rise of intensity with pressure, which they stated was evidence of single collisional excitation processes. They also stated that the sharp rise in intensity above 0.6 torr was due to significant contributions of excitations from secondary processes. This is a

direct contrast to experimental evidence in this paper, Fig. 2 - 9. In fact secondary excitations due to high energy electrons (δ -rays) or soft x-rays were found to be negligibly small at pressures up to 100 torr when compared to the direct excitation to the $(N_2^+)^*$ and (N_2^*) states by protons. And in the 100-800 torr region, secondary excitations of N_2 were found to never be more than about 10% of the total excitation. As Figs. 2-9 indicate, even though the intensity does rise sharply with pressure in the 0-25 torr region, the slope of the curve is always decreasing; not increasing as indicated by Fig. 4(b) of Reeves, Nicholls, and Bromley's paper. The agreement of the theoretical equations developed and the experimental data presented in this paper coupled with the agreement of the calculated reactions rates to those found in the DASA Reaction Rate Handbook [6], indicated that the pressure versus intensity relationship presented in this paper are basically correct. That is, the intensity increased, but at a decreasing rate with increasing pressure above 1 torr due to the collisional de-excitation reaction rate.

C. DISCUSSION

It was found that the second positive band system responded exactly in the same manner to proton bombardment as the first negative band system. This is supported by the excellent agreement of the derived theory and the experimental data and the associated reaction rates obtained. Again these conclusions are in disagreement with Reeves, Nicholls, and Bromley [1] who stated that the second positive band system was excited mainly by secondary electrons. However, the possibility of $(N_2^+)^* + e^- \rightarrow N_2^* + h\nu$ (equation (11)) must be considered. If this recombination rate was large then there would be a formation $(N_2)^*$ from higher

energy $(N_2^+)^*$, term (2) of general equation (1). But comparison of the theoretical curve and the data in Fig. 7 indicates that this recombination rate is small in this case. Thus, the recombination rate must be at least several factors smaller than the collisional de-excitation reaction rate for $N_2^* + N_2 \rightarrow 2N_2$, equation (10).

It was found that the relative intensity of two lines decreased, but not very much, with increasing proton energy. This is the expected behavior, as the excitation cross sections of nitrogen gas are known to decrease with energy [Ref. 13] and to be relatively constant at higher energies. Hence, energy was an important variable, and for each set of experimental data the proton beam energy had to be kept constant. However, even though the curve fitting constants, A and B, varied considerably between experimental data at different beam energies, their ratio (B/A) remained constant. Thus it was deduced that the reaction rates were not energy dependent, but depended only on the absolute temperature and the radiative lifetime of the line in question, as per equation (19).

It is believed that the excitation of N_2 went as equations (2) and (3) and other such methods of excitation of N_2 , such as charge transfer, were very small due to the high energies of the proton beam (1.0 - 2.0 MeV). The absence of any Balmer lines of hydrogen in the observed spectra also would rule out any such charge transfer between the nitrogen or oxygen molecules and the bombarding protons. The lack of these Balmer lines also supports the validity of equations (2), (3), and (4).

All efforts to photograph any lines of the first positive ($B^3\pi_g \rightarrow A^3\Sigma_u^+$) molecular band system failed. The apparatus used to record experimental data also was incapable of detecting any radiation from the first positive system even at pressures as low as 1 torr. The mean lifetime [12]

of the first positive system is on the order of 10^{-4} to 10^{-6} secs. Thus, the reason why first positive radiation could not be detected or photographed was because the collisional de-excitation of excited states of N_2 was much more rapid and pronounced than the radiative decay of excited states of the first positive system.

The radiative lifetimes of molecular oxygen transitions are on the order of from 10^{-3} to 10^{-5} secs. [12] Since the average time between collision in the target chamber, at standard conditions, was about 10^{-9} to 10^{-10} secs. [8], the excited states of oxygen, O_2^* and $(O_2^+)^*$, were collisionally de-excited much more rapidly than possible radiative decay. This explains the inability to photograph the O_2 spectrum, or to detect O_2 transitions with the experimental apparatus. It was assumed that the direct excitation of the O_2 molecules by the high energy protons (H^+) was negligible when compared to N_2 . In view of the long radiative lifetimes of O_2 transitions, this assumption is valid to a high degree.

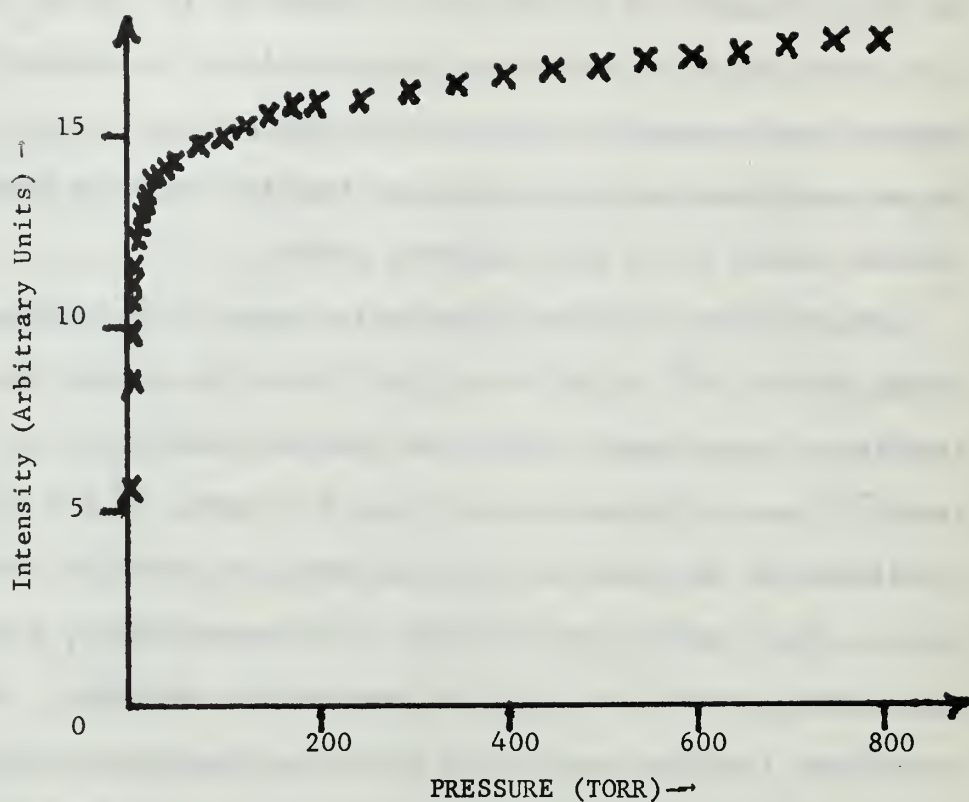


FIGURE 2. Intensity vs. Pressure (3914 \AA). H^+ on N_2

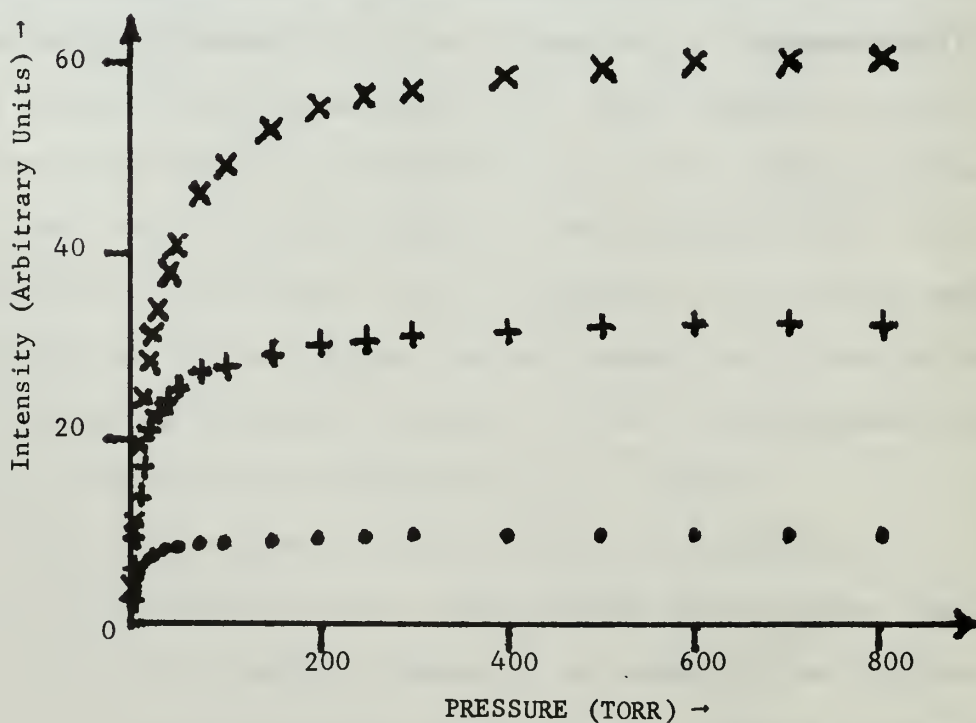


FIGURE 3. Intensity vs. Pressure (3371 \AA). H^+ on 90% N_2 , 10% O_2 (x); 80% N_2 , 20% O_2 ; and 50% N_2 , 50% O_2

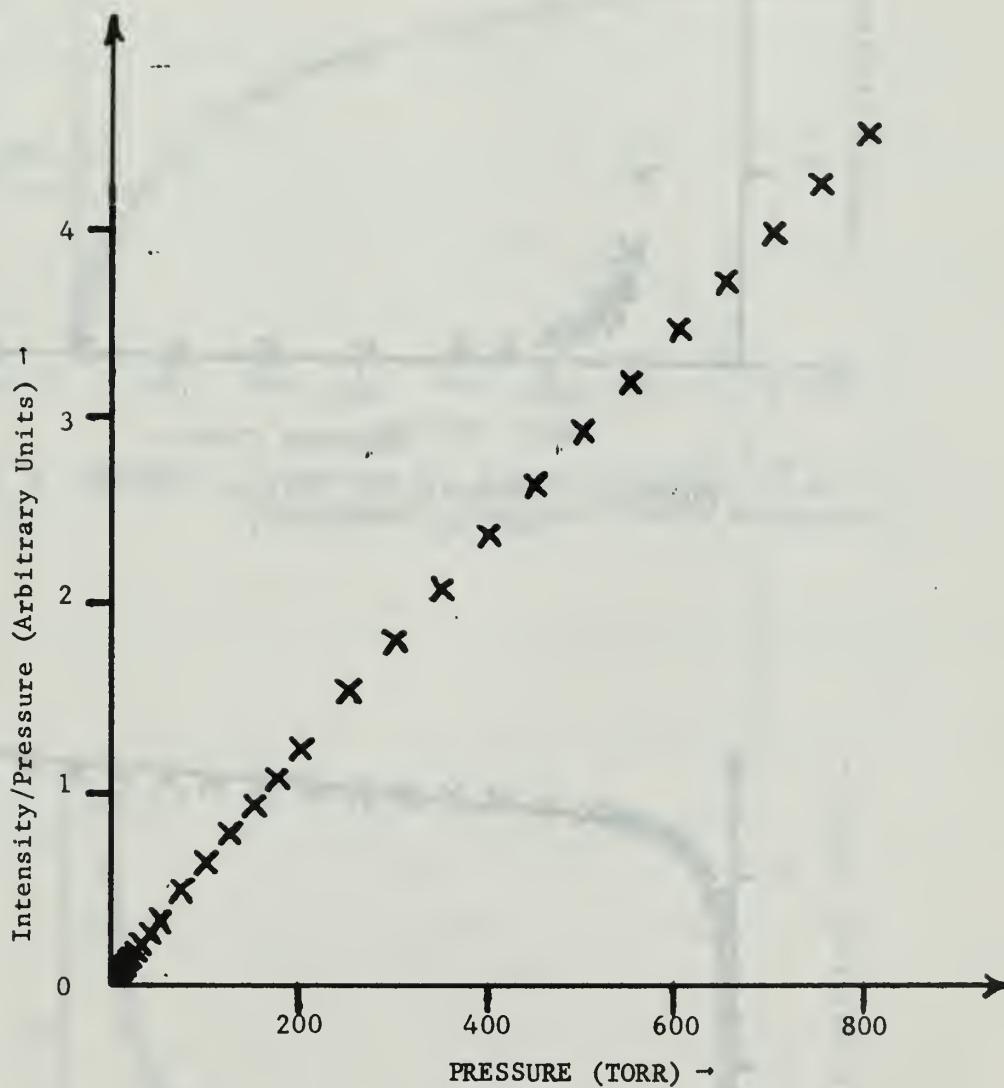


FIGURE 4. Intensity/Pressure vs. Pressure H^+ on N_2 .

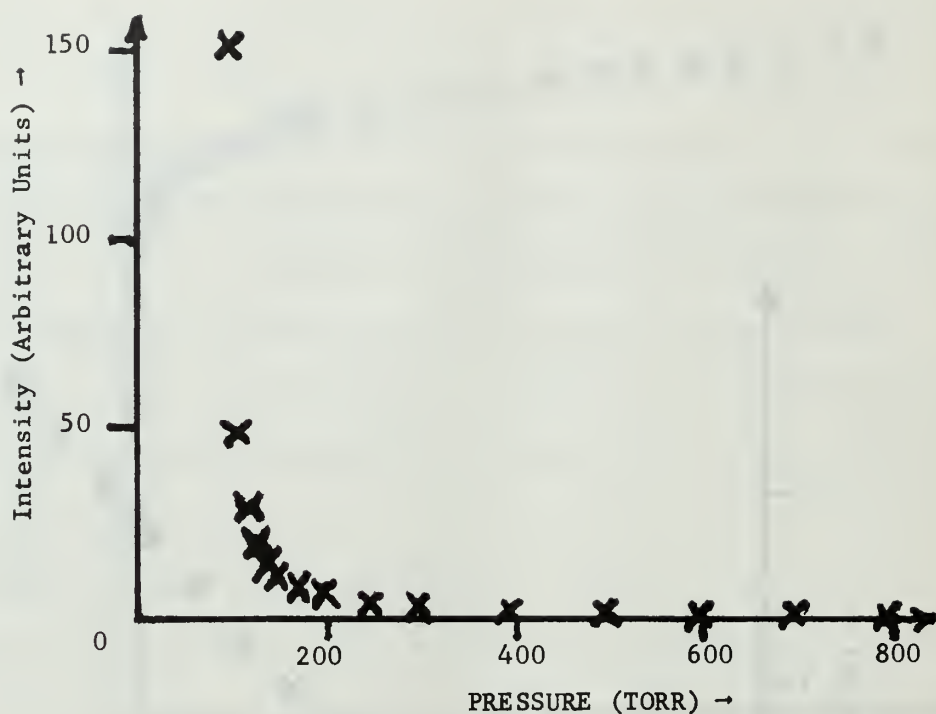


FIGURE 5. Intensity vs. Pressure (3371\AA) H^+ on 100 Torr N_2 , Balance O_2

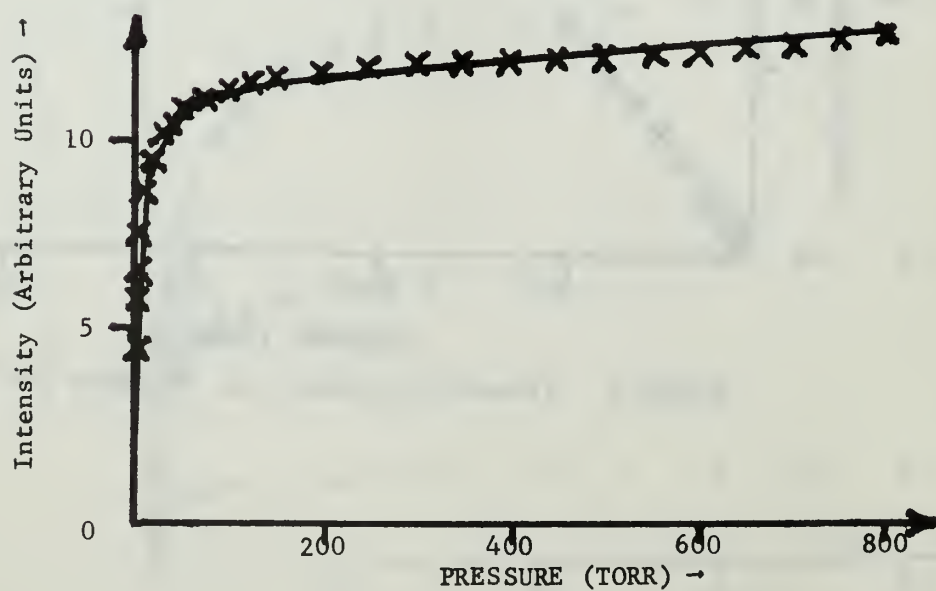


FIGURE 6. Intensity vs. Pressure (3914\AA) H^+ on N_2
Experimental Data (x), Theory Comparison.

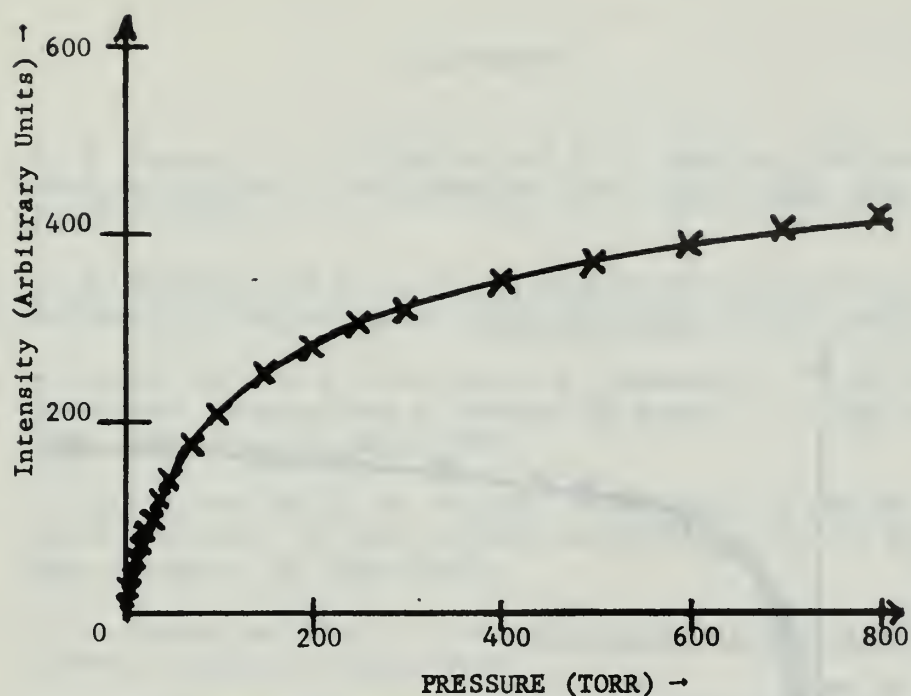


FIGURE 7. Intensity vs. Pressure (3371Å). H^+ on N_2 .
Experimental Data (x), Theory comparison

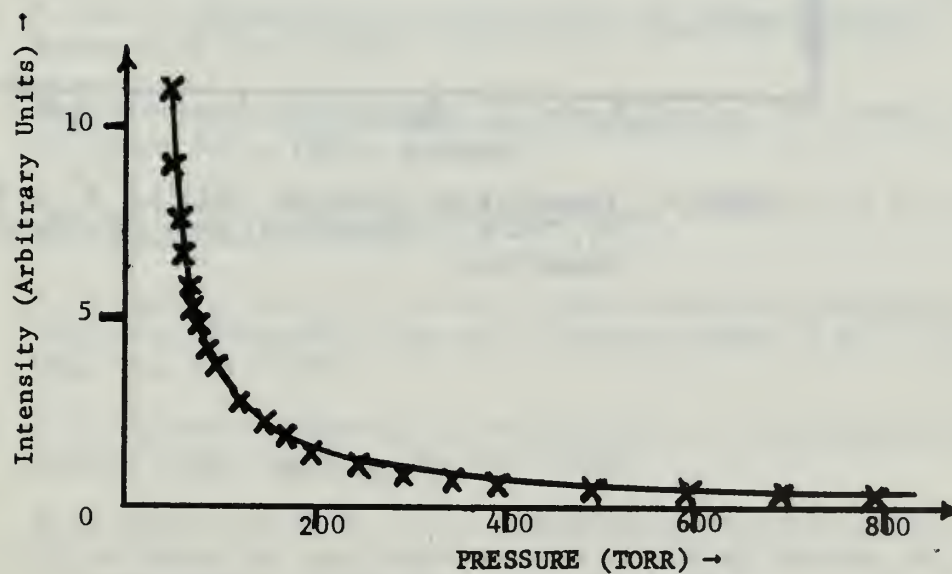


FIGURE 8. Intensity vs. Pressure (3914Å). H^+ on 100 Torr N_2 ,
Balance O_2 . Experimental Data (x), Theory Comparison

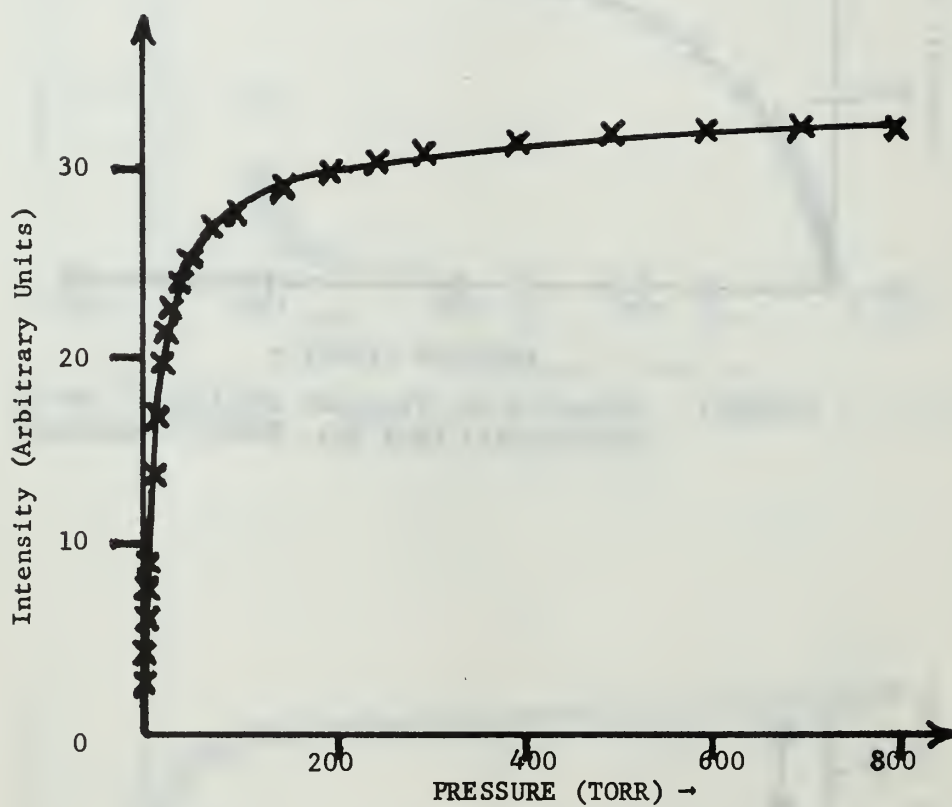


FIGURE 9. Intensity vs. Pressure (3371\AA). H^+ on 80% N_2 , 20% O_2 . Experimental Data (x), Theory Comparison

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13. ABSTRACT

Pure nitrogen and nitrogen-oxygen gas mixtures at pressures from 1 to 800 torr and 300°K were excited by 1.5 MeV protons. Intensity versus pressure data were recorded and plotted for the first negative ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_u^+$) transition ($\lambda = 3914.4\text{\AA}$) and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) transition ($\lambda = 3371.38\text{\AA}$) in nitrogen. Theoretical equations were derived for the intensity as a function of pressure, which were shown to agree quite well with the experimental data. The following reaction rates, k , and de-excitation cross sections, σ , were obtained from the derived theoretical equations and the experimental data: $k = (2.19 \pm 0.29) \times 10^{-10} \text{ cm}^3/\text{sec}$ and $\sigma = (3.25 \pm 0.45) \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $B^2\Sigma_u^+$ state of N_2^+ by N_2 ; $k = (5.70 \pm 0.80) \times 10^{-10} \text{ cm}^3/\text{sec}$ and $\sigma = (8.47 \pm 1.26) \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $B^2\Sigma_u^+$ state of N_2^+ by O_2 ; $k = (7.11 \pm 1.64) \times 10^{-12} \text{ cm}^3/\text{sec}$ and $\sigma = (1.06 \pm 0.25) \times 10^{-16} \text{ cm}^2$ for the de-excitation of the $C^3\Pi_u$ state of N_2 by N_2 ; and $k = (4.62 \pm 0.67) \times 10^{-10} \text{ cm}^3/\text{sec}$ and $\sigma = (6.85 \pm 1.10) \times 10^{-15} \text{ cm}^2$ for the de-excitation of the $C^3\Pi_u$ state of N_2 by O_2 .

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